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Vapor Pressure and Vaporization of Petroleum Fractions

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All major operations of petroleum refining incorporate vaporization and condensation. In this paper methods for computing the vapor pressure and vaporization characteristics of petroleum fractions have been critically reviewed, combined, and extended in order to present a useful compilation of the data and methods now available to the engineer. The use of the modern developments in thermodynamics, including the application of fugacities, is explained by example and checked against experimental results. Short-cut empirical methods are also explained and compared with experimental data.

THE vapor pressure of a liquid at a specified temperature is the pressure under which the liquid is in equilibrium with a vapor. In the case of a pure substance or single component, the liquid and the vapor phases are each of the same composition and composed entirely of the pure substance.

In any case the vapor pressure must be determined of an invariant system—i. e., a system of no degrees of freedom according to the phase rule. In the case of a pure substance or single component it is necessary to fix only the temperature in order to determine the vapor pressure, as the one-component system in two phases has one degree of freedom. In the case of a multiple-component system it is necessary to fix not only the temperature but also the composition in order to have an invariant system. Therefore, it is imperative that no vaporization of a complex liquid be tolerated in determining the vapor pressure of the liquid, as any formation of vapor would change the composition of the liquid whose vapor pressure is being determined. If this precaution is not taken, the vapor pressure determined is not that of the original liquid but rather of the liquid residue remaining after partial vaporization.

EQUILIBRIUM VAPORIZATION

When a mixture of hydrocarbons such as a petroleum fraction is heated to a specified temperature and pressure so that part of the material is vaporized and part is liquid, the process is known as equilibrium vaporization if the resulting vapor and liquid are in equilibrium with each other.

In some cases, as when vapor is formed from the surface of oil in storage, the vapor may not be in equilibrium with the entire body of the liquid owing to inadequate agitation, but in practically all steps in the processing of petroleum there is sufficient agitation to insure approximate equilibrium between vapor and liquid phases. For this reason, as well as the fact that equilibrium conditions are the only conditions that may be duplicated or computed, all calculations presented deal exclusively with equilibrium conditions.

THEORETICAL METHODS

Petroleum fractions are composed essentially of hydrocarbons, and an understanding of the vapor pressure and vaporization characteristics of the hydrocarbons is the necessary basis for a study of the vapor pressure and vaporization characteristics of petroleum fractions.

Vapor pressure data of the paraffin hydrocarbons are fairly complete up to the temperatures of decomposition, but for other types of hydrocarbons the data are scattered and incomplete. In practice it is important to estimate the vapor pressure of these other types of hydrocarbons and the vapor pressure of all types of hydrocarbons at higher temperatures. For these reasons it is necessary to extrapolate and interpolate the available vapor pressure data. Many different methods have been proposed for making these interpolations, all of which are based on the vapor pressure data of the normal paraffin hydrocarbons.

VAPOR PRESSURE DATA

The vapor pressure data are extensive and scattered. Complete data and bibliography up to 1928 on the paraffin hydrocarbons are given by Young (*86*) and by Brown and Coats (*11*). Robinson (*67*) is also a useful source of data and bibliography in addition to the International Critical Tables and other tables of reference. Toluene data are given by Young (*88*) and recently by Krase and Goodman (*40*). Linder (*46*) gives data on a number of hydrocarbons over a limited temperature range in the neighborhood of 0° C. Hexane and heptane data over a limited temperature range are reported by Smyth and Engel (*70*), which are in close agreement with the earlier and more extensive data of Young (*87*).

VAPOR PRESSURE RELATIONSHIPS

As early as 1855 Kopp (*39*) stated that the boiling point at the atmospheric pressure of the adjacent members of a homologous series of liquids differed by a constant amount. This relationship was extended to pressures other than atmospheric by Winkelman (*83*).

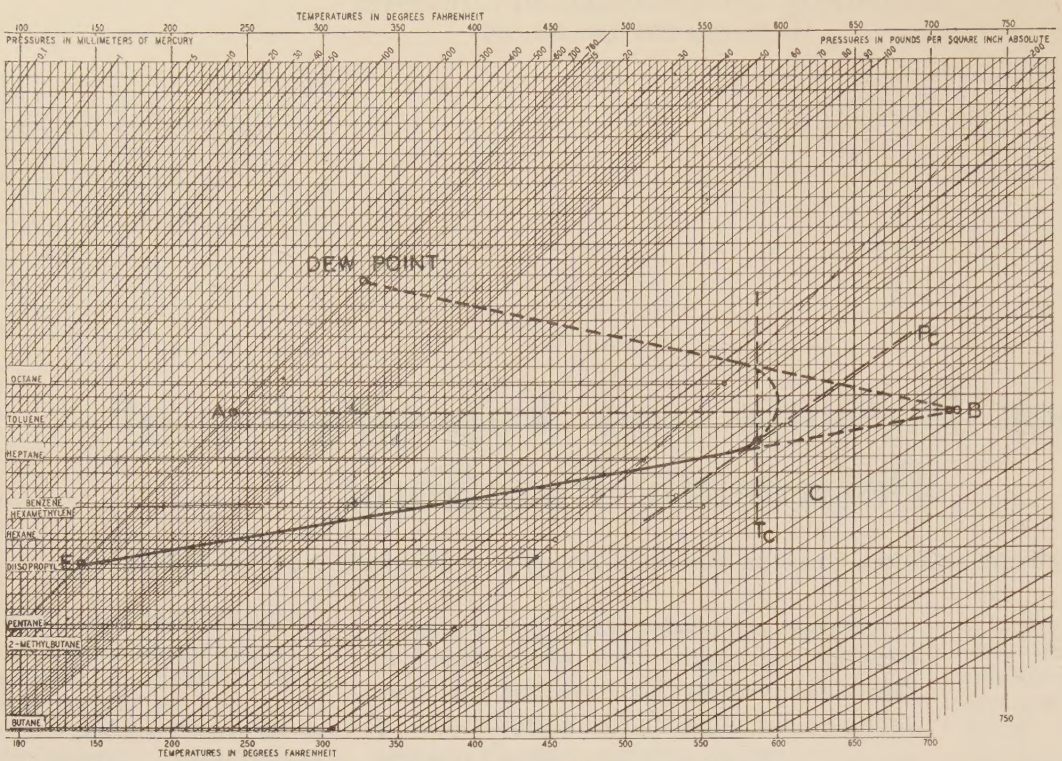

FIGURE 1. PART OF VAPOR PRESSURE CHART

The law of corresponding boiling points introduced by Dühring (*26*, *27*) states that the ratio of the difference between the boiling points of one substance at two different pressures to the difference between the boiling points at the same two pressures of another substance is equal to a ratio of constants which are characteristic of the materials. In practice this ratio between two constants has ordinarily been taken as a single constant. Although this rule does not exactly fit experimental data (*35*), it has served as a basis for many methods of interpolation and of many different properties (*58*).

A more general relationship was given by Ramsay and Young (*65*, *87*):

$$\frac{T_a}{T_b} = \frac{T'_a}{T'_b} + C(T_a - T'_a) \qquad (1)$$

where T_a, T_b = corresponding boiling points (abs.) of compounds a and b at one pressure
T'_a, T'_b = corresponding boiling points (abs.) of compounds a and b at any other pressure
C = a constant

In the same terms Dühring's rule may be written

$$\frac{T_a - T'_a}{T_b - T'_b} = C \qquad (2)$$

Equation 2, deduced from the Clausius-Clapeyron equation, was used for plotting experimental data by Johnston (*34*). A similar derivation may be found by White (*78*).

Several extensions and modifications of the relationships have been studied by other investigators (*18*, *25*, *36*, *45*). Carr and Murphy (*17*) found that Dühring's rule was more satisfactory when applied to related compounds in which case the lines for the different compounds converged approximately at a single point.

A more common form of plotting this same relationship was first suggested by Cox (*21*) who plotted logarithm of the vapor pressure as a function of temperature so that the vapor pressure data of water formed a straight line. Scattered data for the vapor pressure of hydrocarbons were represented approximately by straight lines converging at a common point on this plot. This form of chart was further developed by Ashworth (*3*) from vapor pressure data below one atmosphere by plotting the logarithm of the vapor pressure against an empirically derived function of temperature. A similar plot in which the temperature scale was constructed on the basis of hexane instead of water as in the original Cox plot was prepared by Maxwell (*49*).

The first chart covering a wide range of compounds and pressures was prepared by Wilson and Bahlke (*80*) by plotting the logarithm of the vapor pressure as a function of the logarithm of the absolute temperature for hydrocarbons from C_4H_{10} to $C_{24}H_{50}$, using Hildebrand's theory of parallel curves to extrapolate the available data. These curves were later replotted and extended on a plot, using the coördinates suggested by Cox, by Calingaert and Davis (*15*); these in turn were used by Wilson (*79*) for the construction of a nomograph or alignment chart for the vapor pressure of the normal paraffin hydrocarbons.

Many other relationships have been suggested (*1*, *5*, *37*, *55*) but appear less convenient for the present purpose.

In the first complete critical correlation of vapor pressure data of normal paraffin hydrocarbons Young (*86*) calculated and leveled the boiling point data by three methods—a modification of Kopp's boiling point rule (*85*), the Ramsay-Young rule (*65*), and a plot of the log of the boiling point as a function of the log of the number of carbon atoms. Brown and Coats (*11*) presented an empirical method for leveling the vapor pressure data of normal paraffin hydrocarbons based on all available data and included a chart of the vapor pressures of these compounds from propane through heptane, in which the vapor pressure of any normal paraffin hydrocarbon is represented by a straight horizontal line.

Since the various log plots do not yield straight lines (*20*) and the lines do not intersect in a common point as has been assumed in their construction, an extension of the Brown-Coats chart to cover the entire range of hydrocarbons has been found accurate, in good agreement with subsequent data, and convenient in use. Figure 1 is a part of this chart on a reduced scale.[1] The vapor pressures of normal paraffin hydrocarbons are represented by straight horizontal lines. The vapor pressures of other pure hydrocarbons are represented by straight lines approximately horizontal, so that the vapor pressure of any pure hydrocarbon may be represented by a straight horizontal line without serious error.

[1] The complete chart may be obtained from G. G. Brown at a cost of $1.00.

Mixture of Hydrocarbons

In treating mixtures of hydrocarbons it has been the usual practice in the past to assume the validity of Raoult's (*66*) and Dalton's (*23*) laws, by means of which it is possible to calculate equilibrium vaporization of mixtures from the vapor pressure data as included in a vapor pressure chart and the composition of the mixture. When treating compounds at temperatures above the critical, it is then necessary to extrapolate the vapor pressure curve beyond the critical temperature and use this extrapolated value as vapor pressure in the following equation:

$$\frac{y}{x} = \frac{p}{P} = K \tag{3}$$

where y = mole fraction of the hydrocarbon in vapor
x = mole fraction of the hydrocarbon in liquid in equilibrium with vapor
p = vapor pressure of pure liquid hydrocarbon at equilibrium temperature
P = total pressure on system
K = equilibrium constant for the hydrocarbon at equilibrium temperature and pressure

Clearly the value of K in this equation depends entirely upon the hydrocarbon, the temperature, and the pressure of the equilibrium.

The vapor pressure of a known liquid mixture of hydrocarbons at any temperature is readily calculated as the sum of the products of the mole fractions by the corresponding vapor pressures at the indicated temperature:

$$\text{Vapor pressure} = \Sigma(xp) \tag{4a}$$

Or by trial and error, when using the equilibrium constants K, until the correct value for P is found, when

$$\Sigma(xK) = 1 \tag{4}$$

The bubble point, or temperature at which vapor will begin to form from a known liquid mixture at any pressure, may be calculated by a trial and error method in which the vapor pressures, or equilibrium constants, K, of the individual hydrocarbons are determined for an assumed temperature, and the vapor pressure of the mixture computed for the assumed temperature; the proper solution is readily obtained by graphical interpolation, using the vapor pressure curve of the mixture so computed by Equations 4 or 4a to indicate the temperature at which the mixture has the desired vapor pressure.

The dew point of a known vapor mixture, or temperature of initial condensation at any pressure, may be calculated (*32*) by trial and error as the temperature at which

$$\Sigma\left(\frac{p}{y}\right) = P \tag{5a}$$

or

$$\Sigma\left(\frac{K}{y}\right) = 1 \tag{5}$$

This method may be used to include mixtures of hydrocarbon vapor with air or other gases.

Equations 5 and 5a may also be used to determine the pressure, P, of initial condensation of a known vapor at any temperature. In this case Equation 5a may be solved directly, but trial and error methods must be used for Equation 5.

The quantity vaporized and the quality of the vapor and liquid formed under equilibrium conditions at a stated temperature and pressure from a mixture or feed of known composition may be calculated as follows:

By a material balance,

$$F = V + L \tag{6}$$

By a material balance for each hydrocarbon,

$$zF = yV + xL \tag{7}$$

where F = total moles of feed, or total material
V = total moles of vapor formed in the equilibrium vaporization
L = total moles of liquid formed under equilibrium
x = mole fraction of the hydrocarbon in liquid
y = mole fraction of the hydrocarbon in the vapor
z = mole fraction of the hydrocarbon in the feed

Substituting y/k for x in Equation 7 and solving for y gives:

$$y = \frac{zF}{V + \frac{L}{K}} = \frac{F}{V}\left(\frac{Kz}{K + \frac{L}{V}}\right) \tag{8}$$

Similarly, substituting Kx for y and solving for x gives

$$x = \frac{F}{V}\left(\frac{z}{K + \frac{L}{V}}\right) \tag{9}$$

Since the sum of the mole fractions of all the hydrocarbons in the liquid equals unity and the sum of the mole fractions of all the hydrocarbons in the vapor equals unity,

$$\Sigma y = 1 = \frac{F}{V}\Sigma\frac{Kz}{K + \frac{L}{V}} \tag{10}$$

$$\Sigma x = 1 = \frac{F}{V}\Sigma\frac{z}{K + \frac{L}{V}} \tag{11}$$

olving for V/F from each equation gives

$$\frac{V}{F} = \Sigma\frac{Kz}{K + \frac{L}{V}} = \Sigma\frac{z}{K + \frac{L}{V}} \tag{12}$$

The values of K are for each hydrocarbon at the temperature and total pressure of the equilibrium.

The quantity vaporized is found by trial and error by assuming a value of V for any desired quantity of feed, F, and determining the values for either summation in Equation 12. This is done by determining the value of the expression for each hydrocarbon and adding all of these values to determine the value of the summation. The correct solution has been obtained when the value of the summation is equal to the assumed value for V/F. Usually the results of two or three trials may be plotted against the assumed value for V/F and the solution obtained by interpolation.

The quality of the vapor, and liquid, expressed in terms of mole fraction, is readily obtained by use of Equations 8 and 9 for each of the hydrocarbons.

Similar methods have been used by Murray (*52*) and others (*59*, *60*, *68*).

Complex Mixtures

Complex mixtures may be considered as a mixture of close-cut fractions, each of which has the properties of a pure hydrocarbon, and treated in the manner described, or the same relationships may be used in the differential form and applied to complex mixtures in which the composition may be expressed as a true boiling point curve as obtained from an efficient column distillation in the laboratory, in terms of components identified by their boiling points.

Since it is required that the composition of the mixture be expressed in terms of mole fraction, it is necessary to convert the true boiling point curve from a weight to a molecular basis. This may be done by considering the whole sample as composed of a number of close-cut fractions, as obtained by dividing the true boiling point curve of the entire sample into a number of arbitrary fractions. Each of these close cuts has a molecular weight which may be determined from its average boiling point by means of a curve of molecular weight *vs.*

average boiling point as determined experimentally on a number of cuts from the sample (*29*, *68*, *77*), or by means of the average boiling point and the gravity as suggested by Watson (*76*). If the source of the material is known, the molecular weight may be determined as a function of the average boiling point as indicated in Figure 2, constructed from data in the literature and from private sources (*71*). The weight of each close-cut fraction per unit weight of total sample is divided by the molecular weight of the fraction to determine the

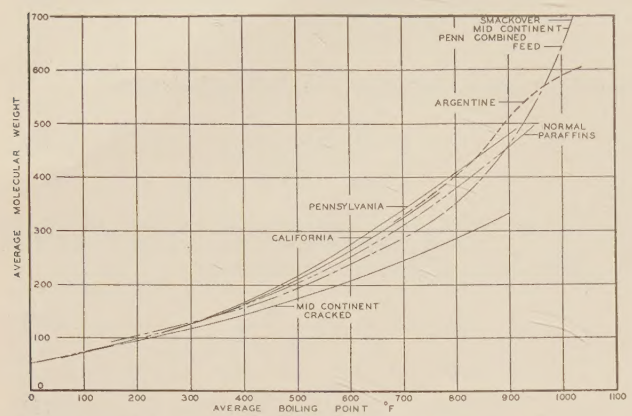

FIGURE 2. MOLECULAR WEIGHTS OF FRACTIONS OF TYPICAL CRUDES

number of moles. The mole fraction in each of the close-cut fractions is then determined by dividing the number of moles in the fraction by the total number of moles in the unit weight of the whole sample. From these data and the boiling range of each fraction a true boiling point curve may be constructed, expressed in terms of mole fraction and used to indicate the molecular composition of the sample (Table III gives actual computations).

The above equations derived for mixtures of individual hydrocarbons may be put into the differential form:

$$\int dx = \frac{F}{V} \int \frac{1}{K + \frac{L}{V}} dz \qquad (13)$$

$$\int dy = \frac{F}{V} \int \frac{K}{K + \frac{L}{V}} dz \qquad (14)$$

where dx, dy, dz = mole fraction of the differential component boiling between $T°$ and $(T + dT)°$ as defined by the molecular true boiling point curve as described above

In these equations the properties of the complex mixtures are assumed to be continuous—i. e., form a smooth curve throughout the entire range of composition, enabling one to use the data and properties of the pure hydrocarbons for any point on the true boiling point curve. These equations may be integrated graphically between the limits of $z = 0$ and $z = 1$ by plotting the expression $[1/(K + L/V)]$ or $[K/(K + L/V)]$ as a function of z, using as many points as desired to obtain the required accuracy in the curve. This integral must equal V/F since the integral of dy and of dx must be equal to 1 when integrated between the corresponding limits. This graphical method may be applied in exactly the same manner as has been described for the method of summations in computing the quantity of vapor and liquid formed in an equilibrium vaporization.

The quality of the liquid and vapors are also obtained in a similar manner (*59*). When the proper values of L and V have been inserted in the equation, the integral curve multiplied by F/V gives x or y as a function of z. Since the boiling point is known as a function of z from the true boiling point curve of the feed, the true boiling point curve of the liquid or vapor may be readily constructed by plotting boiling point as a function of x or y. (A complete example will be given at the end of this discussion.)

From these equations the vapor pressure, dew point, bubble point, and equilibrium vaporization may be calculated almost as readily for complex mixtures as for mixtures of individual hydrocarbons.

For complex mixtures,

$$\int dy = \int K dx \qquad (15)$$

which may be used in exactly the same way as $\Sigma y = \Sigma Kx$ for determining vapor pressure, bubble point, and dew point, as has been described for mixtures of hydrocarbons.

It has been shown (*16*, *68*, *82*) that Raoult's and Dalton's laws are not exact even in relatively simple mixtures of hydrocarbons. Brown and Caine (*10*) have used methods similar to those described for determining an over-all correction factor which may be used to multiply K in the above expression to give results concordant with experimental data. These correction factors varying from 0.86 to 0.9 were determined by calculating the quality of the liquid in equilibrium with the vapor and comparing the calculated quality with the experimentally determined distillation curve. If these over-all correction factors as determined for the California naphtha are used to determine the quantity of vapor formed in an equilibrium vaporization, the results are less satisfactory than if the uncorrected Raoult's law was used as indicated in Table IV.

More recent data at high pressures indicate still greater deviations from Raoult's and Dalton's laws. This is to be expected since these laws are based upon the assumption of ideal gases and the assumption that the vapor pressure of a liquid component is dependent upon temperature alone, both of which introduce important errors, particularly at high pressures.

EFFECT OF PRESSURE ON VAPOR PRESSURE

The vapor pressure of a liquid is always determined under a total pressure, equal, by definition, to the vapor pressure. In the presence of additional components, not present in the liquid phase whose vapor pressure is desired, the total pressure may differ widely from the vapor pressure of the liquid. Under such conditions the effect of total pressure on the vapor pressure should not be neglected.

This so-called Poynting effect (*62*) has been demonstrated (*42*, *47*, *61*) and derived from thermodynamic considerations (*30*, *44*). Using modern nomenclature, for equilibrium at constant temperature and for an increase in total pressure:

$$\Delta F_L = \Delta F_V \qquad (16)$$

$$\int_{p_0}^{P} v dP = \int_{p_0}^{p} V dp \qquad (17)$$

where v = molal volume of liquid
V = molal volume of vapor
P = total pressure on liquid
p = vapor pressure, or pressure of vapor in equilibrium with liquid
p_0 = normal vapor pressure at the constant temperature

The molal volume of the liquid may usually be assumed constant, and, if the vapor may be assumed to be ideal:

$$\ln \frac{p}{p_0} = \frac{v}{RT} (P - p_0) \qquad (18)$$

With these assumptions the vapor pressure of pentane at 40° C. is increased by 19.6 per cent when the total pressure is increased to 40 atmospheres. Making partial correction for deviations from the ideal gases by assuming the compressi-

bility factor of the vapor to be constant at the value of the normal vapor pressure, the vapor pressure is increased by 20.9 per cent with an increase in total pressure to 40 atmospheres.

This method of correcting the vapor pressure is of little practical value because of the double integration and the necessary assumptions. Use of the assumption of ideal solutions and the fugacity as proposed by Lewis and Randall (*44*) and applied to hydrocarbons by others (*14*, *43*) offers a more satisfactory method of reducing the errors involved in the assumption of Dalton's and Raoult's laws.

Fugacities and Ideal Solutions

The pressure-volume-temperature data necessary for computations of fugacities for hydrocarbon vapors are incomplete. The data for methane (*41*), ethylene (*2*), isopentane (*85*), *N*-pentane (*69*), hexane (*73*), and octane (*64*) have been found. By use of the theorem of corresponding states (*57*), it is possible to interpolate and to extrapolate these data to include a wide range of hydrocarbons. Cope, Lewis, and Weber (*19*) have used the deviations of ethylene for hydrocarbons of more than two carbon atoms. Brown, Souders, and Smith (*14*) have indicated a trend in the deviation from ideal gases which is a function of molecular weight. Comparison of this plot based on data of methane, isopentane, and *N*-pentane with data on hexane and octane verifies the existence and approximate magnitude of this trend.

The fugacity of any vapor may be computed from the compressibility factor by integration of the equation:

$$\ln f = \ln P - \int_0^P \frac{1 - Z}{P}\, dP \qquad (19)$$

where $Z = \frac{PV}{RT}$, the compressibility factor

Critical temperatures and critical pressures of a compound are necessary in order to use the compressibility factor for determining pressure-volume-temperature data or fugacity. The data on compounds from methane through octane have been tabulated (*14*). Numerous relationships for estimating critical temperatures from other physical properties have been suggested, but many of the required properties are not readily available (*24*, *31*, *33*, *38*, *74*, *89*). McKee and Parker (*51*) proposed the empirical equation:

$t_c = 1.5\, t_b + 286$, for aliphatic and naphthenic materials (20)
$t_c = t_b + 373$, for aromatic material (21)

where t_c = critical temperature, ° F.
t_b = normal boiling point, ° F.

When using Centigrade temperatures the constants are 160 and 208 instead of 286 and 373, respectively.

Watson (*75*) developed a more accurate relationship based on normal boiling point, density at the boiling point, and molecular weight. A more convenient chart by Eaton and Porter (*28*) gives critical temperatures as a function of boiling points and density or ° A. P. I. gravity. Recently Watson (*76*) has simplified his earlier relationship, making a more convenient method for estimating the critical temperature.

The critical pressure can be determined from the vapor pressure characteristics as indicated by the vapor pressure chart (Figure 1), the critical temperature, and boiling point. For pure hydrocarbons or close-cut fractions the vapor pressure curve is extended as a horizontal line through the boiling point and indicates directly the critical pressure at the critical temperature.

For mixtures the following procedure may be used as approximately correct: Use either the molal average boiling point (*76*) or the 50 per cent point on the equilibrium vaporization curve at 760 mm. and draw a horizontal line, *AB*, on

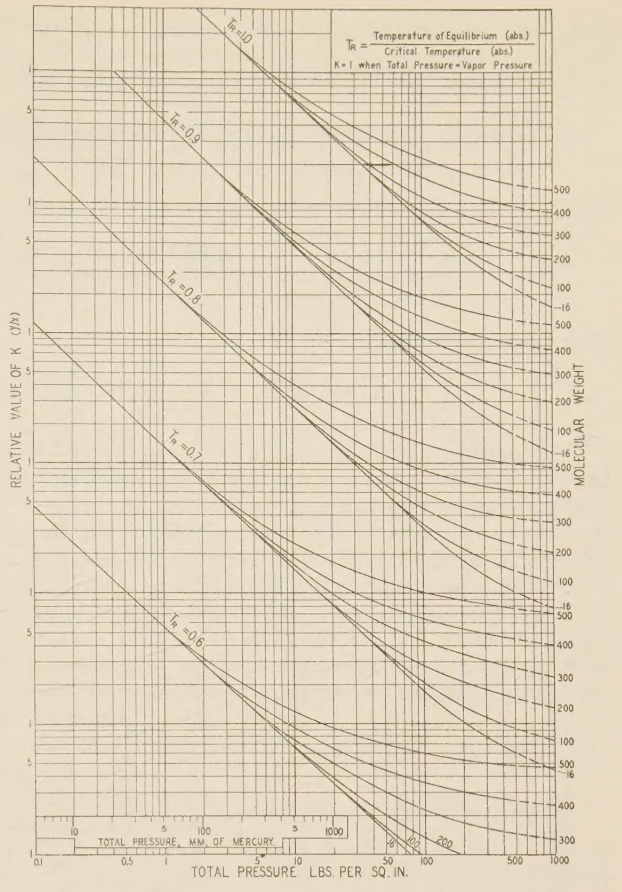

Figure 3. Relative Values of Equilibrium Constants, K

the vapor pressure chart (Figure 1) through this average boiling point, *A*, extending past the critical temperature (T_c) a distance 0.3 (that between *A* and T_c). A straight line, *EB*, drawn through the bubble point, *E*, of the fraction and point *B* will intersect the critical temperature, T_c, at approximately the critical pressure, P_c.

Usually the vapor pressure line, *EC*, should be curved slightly before reaching the critical point, *C*, so that the critical pressure line, P_c, is tangent to the vapor pressure line at the critical point, *C*.

The fugacity of a liquid under its own vapor pressure is equal to the fugacity of the vapor. Under any other pressure the fugacity of the liquid is not the same as that of the saturated vapor but may be readily calculated (*14*) from the density of the liquid (*87*).

$$\ln \frac{f_P}{f_{p_0}} = \frac{1}{RT} \int_{p_0}^{P} v\, dP \qquad (22)$$

where f_{p_0} = fugacity of liquid or vapor under normal vapor pressure
f_P = fugacity of liquid under a total pressure of P
p_0 = normal vapor pressure
P = total pressure
v = molal volume of liquid

Relationship of Ideal Solutions

The ideal solution is defined (*44*) as a solution in which fugacity of each component is proportional to the mole fraction of that component. This generalized statement of Raoult's law makes correction for deviation from the ideal gases and also for the effect of pressure on the vapor pressure of a liquid. It implies among other things that the volume and the heat content are additive; this has been verified within certain

limits for hydrocarbons of the same type by experimental data (*88*). Although not exact, this assumption is far more satisfactory than that of Raoult's and Dalton's laws as ordinarily used.

This statement of the ideal solution may also be stated as:

$$xf_L = yf_V \qquad (23)$$

where x, y = mole fractions of the component in the liquid and vapor, respectively
f_L, f_V = fugacities of the pure liquid and pure vapor, respectively, at the temperature and total pressure of the equilibrium

With these assumptions:

$$K = \frac{y}{x} = \frac{f_L}{f_V} \qquad (24)$$

The logarithms of these equilibrium constants, K, so defined have been plotted as a function of the logarithm of the total pressure for constant reduced temperature (ratio of the absolute temperature to the absolute critical temperature) for paraffin compounds from methane to pentane, inclusive (*14*). The lines are straight and parallel at the lower pressures and for the low molecular weight hydrocarbons. At higher pressures and for the higher molecular weights the lines become curved concavely upward. The form of the chart is well adapted for extrapolation which is necessary for the higher molecular weight fractions. By plotting the relative values for the equilibrium constants instead of the absolute values, these lines become superimposed except for the increasing curvature for the higher molecular weights at the higher pressures. This curvature has been extrapolated as a straight-line function of molecular weights and the relative values for K for hydrocarbons up to 500 molecular weight plotted as shown in Figure 3. The values for the higher molecular weights are uncertain, but the chart is considered reliable for molecular weights up to about 200 and is the best means available for extrapolating these data to include compounds of higher molecular weight.

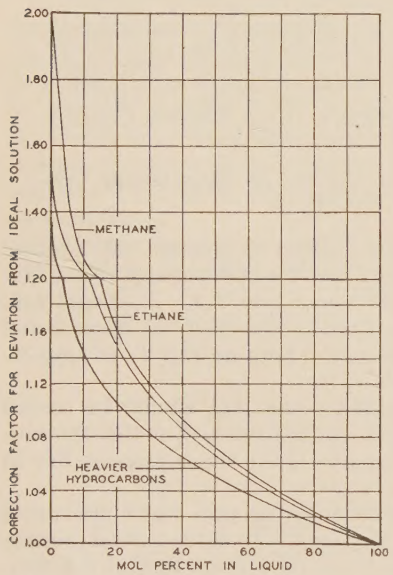

FIGURE 4. MULTIPLY VALUE OF EQUILIBRIUM CONSTANT, K, BY CORRECTION FACTOR ACCORDING TO MOLE FRACTION IN THE LIQUID AS INDICATED IN THIS FIGURE

In order to find the value of K for any component at any temperature and pressure, it is necessary to know the molecular weight, the critical temperature, and the vapor pressure characteristics of the compound. By definition K is unity when the vapor pressure, p, equals the total pressure. The value of K for each and every component in a mixture is also equal to unity at the critical point of the mixture. This fact must be considered and the values of K modified accordingly near the critical point of a mixture.

The value of K for any component may be found as follows: Determine the vapor pressure of the component at the desired temperature of the equilibrium from a boiling point of the component by the vapor pressure chart (Figure 1). Using Figure 3, choose the curve corresponding to the molecular weight of the component and the reduced temperature at which the value of K is desired. The intersection of this curve with the pressure abscissa equal to the vapor pressure of the component at this temperature determines the ordinate which has unit value ($K = 1$). The scale of K along the ordinate is entirely relative and must be given absolute value for each determination in this manner. Set a pair of dividers to the difference between the ordinate of this point of intersection and the ordinate indicated as unity on the K scale shown in Figure 3. Lay off this same length, or difference in ordinates, from the curve at any desired total pressure to read the value of K for that total pressure directly on the K scale of the figure.

The values for K determined by this means may be used for determining vapor pressure, dew points, bubble points, and the quantities and qualities of liquid and vapor formed in equilibrium vaporization in the same manner as has been described in Equations 3 to 15.

From the method of derivation, the values of K as given should be most reliable when applied to components present in high concentrations. Corrections for deviations from the ideal solution may be readily applied when available.

Brown and Souders (*13*) report an apparent positive deviation of almost 100 per cent for methane present in low concentrations in absorption oil. Recently Matheson and Cummings (*48*) have determined the deviation in Raoult's law at low pressure as a function of concentration of the paraffin hydrocarbon in an absorption oil. These deviations are largely deviations from ideal solutions and may be used as such for correcting the values of K. The corrections indicated in Figure 4 represent the best available data on the deviation from ideal solutions and may be used to correct values of K for concentration, particularly of the more volatile components in the liquid phase. This is done by multiplying the value of K by the correction factor as indicated in Figure 4 according to the molecular percentage of the component in the liquid. This correction is important when dealing with natural gasoline and gaseous components but does not appear so necessary for the higher molecular weight components encountered in heavy oils. This may be due to greater accuracy of the plots and of analytical methods when applied to gases and gasoline components.

Accuracy of Equilibrium Constants

The approximate accuracy of the values of K for the more volatile hydrocarbons has been checked by comparison with reflux and residue gas from natural gasoline rectifiers. Data from a recent publication (*63*) are compared in this way with the computed equilibrium conditions at 75° F. and 268 pounds per square inch absolute.

Although the values for K may be determined from Figure 3 in the manner indicated, the use of charts which give K directly for any temperature and pressure are far more convenient. For this reason working charts for methane, ethane, propane, isobutane, *N*-butane, isopentane, *N*-pentane, hexane, heptane, decane, tetradecane, nonadecane, and triacontane, covering all pressures up to 500 pounds per square inch and working temperatures up to 1000° F., have been prepared.[2] By plotting log K as a function of boiling point for any particular equilibrium, values for intermediate fractions may be obtained by interpolation of the values read from these charts in a more satisfactory manner than reading from Figure 3. Figures 5 and 6 represent parts of the pentane and heptane charts and indicate how these charts may

[2] A complete set of these charts may be obtained from G. G. Brown at a cost of $3.00.

be used to compute equilibrium conditions of mixtures even in the neighborhood of the critical point where the ideal solution laws break down.

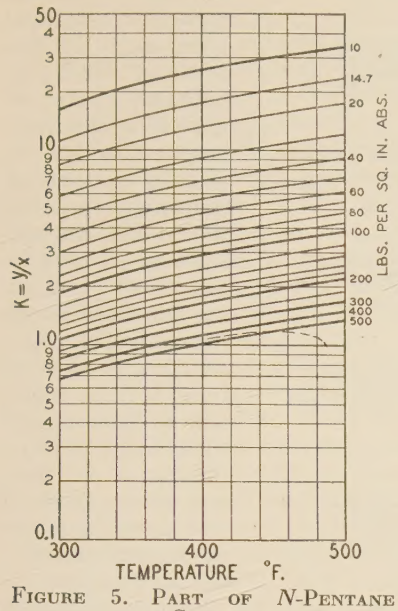

FIGURE 5. PART OF *N*-PENTANE CHART

The values for K given in column 7 of Table II were read directly from Figures 5 and 6. The values given in column 8 are these values multiplied by the factor as indicated in Figure 4, except for pressures of 444 pounds per square inch which is the critical pressure for a mixture containing 25.5 per cent of pentane. Since the value of K becomes unity for each component at the critical point, the equilibrium charts have been modified by making the values of K unity at 444 pounds and 488° F. by drawing in the dash line as shown in Figures 5 and 6. Values read from these dash lines and modified by the factors of Figure 4 are given in column 7 for pressures of 444 pounds per square inch.

TABLE I. COMPARISON OF CALCULATED AND EXPERIMENTAL EQUILIBRIUM CONSTANTS FOR VOLATILE HYDROCARBONS

(At 75° F. and 268 pounds per square inch absolute pressure)

	By Analysis (*63*)			Calculated y/x		
Component	In residual gas, y	In residual flux, x	y/x	By Raoult's law	By K from Fig. 3[a]	K cor. by Fig. 4
	Mole fraction					
CH_4	0.393	0.027	14.6	35.	8.2	14.3
C_2H_6	0.257	0.125	2.06	2.2	1.63	1.96
C_3H_8	0.261	0.46	0.567	0.5	0.6	0.63
$Iso C_4H_{10}$	0.088	0.374	0.235	0.186	0.27	0.288
C_4H_{10}				0.127	0.20	0.214
C_5H_{12}	0.001	0.014	0.07	0.035	0.066	0.078

[a] The same values may be obtained directly from published charts (*14*).

These data given as for normal paraffin hydrocarbons also include considerable quantities of unsaturated compounds. The agreement between the values for y/x computed by the ideal solution relationship as obtained from Figure 3 and the values obtained from actual analysis is generally satisfactory, and much better than between Raoult's law and actual analysis. The corrections for deviations from ideal solutions as given in Figure 4 modify the values as shown in the last column, which are very close to the experimental values.

Another interesting comparison (Table II) is provided by recent data of Cummings, Stones, and Volante (*22*) on pentane-heptane mixtures up to the critical conditions.

The necessity for correcting the values of K to unity at the critical point of the mixture is clearly evident. The behavior of pentane agrees closely with the predicted values, but heptane at the critical pressure appears slightly more volatile than would be expected from computed values.

CALCULATION OF VAPORIZATION OF COMPLEX MIXTURES

The application of these equilibrium constants to the calculation of equilibrium vaporization may be explained by application to data from the literature (*10*). The distillation curves of the California heavy naphtha and of the liquid and vapor formed from its partial vaporization were obtained from the original unpublished record, and molecular weights from the data of Figure 2.

TABLE II. COMPARISON OF EXPERIMENTAL (*22*) AND CALCULATED EQUILIBRIUM CONSTANTS FOR *N*-HEPTANE AND *N*-PENTANE AT HIGH TEMPERATURES AND PRESSURES

		Experimental			Calculated y/x		
Pressure	Temp.	Vapor, y	Liquid, x	y/x	By Raoult's law	By K from Fig. 5	K cor. by Fig. 4 and for critical conditions
Lb./sq. in.	° F.	*Mole %*					
				PENTANE			
147	375	24	10	2.4	3.0	1.9	2.17
	356	41.7	20	2.08	2.6	1.75	1.93
	339	55	30	1.83	2.2	1.64	1.77
	324	65.8	40	1.65	1.95	1.53	1.64
	310	74.4	50	1.49	1.7	1.49	1.57
	297	81.3	60	1.36	1.5	1.31	1.36
	286	86.8	70	1.24	1.35	1.24	1.275
	276	91.8	80	1.15	1.22	1.13	1.15
	267	96.1	90	1.07	1.10	1.06	1.07
294	456	17	10	1.7	2.9	1.53	1.74
	438	32.2	20	1.61	2.5	1.47	1.61
	422	44.7	30	1.47	2.2	1.4	1.51
	406	56.2	40	1.40	1.9	1.32	1.42
	390	66.3	50	1.326	1.7	1.26	1.33
	377	75.5	60	1.26	1.6	1.21	1.26
	364	83.2	70	1.19	1.4	1.15	1.18
	351	89.9	80	1.122	1.2	1.10	1.12
	340	95.2	90	1.058	1.1	1.04	1.05
444	488	25.5	25.5	1.0	2.5	1.38	1.0
	480	33.7	30	1.12	2.3	1.35	1.1
	463	46.3	40	1.16	2.0	1.3	1.15
	447	57.7	50	1.15	1.8	1.23	1.15
	432	67.7	60	1.13	1.6	1.18	1.13
	417	76.9	70	1.10	1.4	1.13	1.1
	402	85.4	80	1.07	1.3	1.06	1.08
	372	93.2	90	1.04	1.0	0.99	1.00
				HEPTANE			
147	375	76	90	0.844	0.81	0.85	0.85
	356	58.3	80	0.729	0.66	0.73	0.74
	339	45	70	0.643	0.56	0.64	0.66
	324	34.2	60	0.57	0.47	0.565	0.585
	310	25.6	50	0.512	0.40	0.50	0.515
	297	18.7	40	0.467	0.35	0.46	0.49
	286	13.2	30	0.44	0.30	0.38	0.41
	276	8.2	20	0.41	0.26	0.345	0.38
	267	3.9	10	0.39	0.23	0.315	0.36
294	456	83	90	0.92	0.84	0.92	0.92
	438	67.8	80	0.847	0.72	0.84	0.85
	422	55.3	70	0.79	0.63	0.77	0.79
	406	43.8	60	0.73	0.54	0.70	0.73
	390	33.7	50	0.674	0.47	0.64	0.674
	377	24.5	40	0.61	0.41	0.58	0.615
	364	16.8	30	0.56	0.36	0.54	0.58
	351	10.2	20	0.51	0.31	0.48	0.53
	340	4.8	10	0.48	0.28	0.45	0.51
444	488	74.5	74.5	1.0	0.72	0.88	1.0
	480	66.3	70	0.947	0.68	0.85	0.95
	463	53.7	60	0.895	0.59	0.78	0.90
	447	42.3	50	0.847	0.52	0.73	0.80
	432	32.3	40	0.808	0.45	0.685	0.73
	417	23.1	30	0.77	0.40	0.66	0.69
	402	14.6	20	0.73	0.34	0.57	0.65
	372	6.8	10	0.68	0.26	0.47	0.56

Table III indicates all the steps required in a calculation of the quantities and qualities of liquid and vapor formed in an equilibrium vaporization from a weight per cent true boiling point curve, including check computations. The first seven columns indicate the calculations for converting weight per cent into mole fractions in the manner described. In column 8 the normal vapor pressures of the components are given at the temperature of equilibrium as determined from the normal boiling points in column 2 and the vapor pressure chart (Figure 1). Critical temperatures, obtained by Equation 20 (because gravities of the fractions were not recorded), were converted to reduced temperatures by dividing 810.6° Rankine by the corresponding critical temperatures and are recorded in column 9.

The molecular weights of the components are listed in column 10, determined from the normal boiling points (Figure 2) as given in column 2. The molecular weights recorded in column 5, determined from average boiling points in column 4, are of the close-cut fractions used in converting weight to mole per cent and not of the components used in the equilibrium vaporization calculation.

The equilibrium constants, K, at the temperature and pressure of equilibrium were determined from Figure 3 using the

TABLE III. CALCULATION OF EQUILIBRIUM VAPORIZATION OF CALIFORNIA HEAVY NAPHTHA

(760.4 mm. pressure, 350.6° F.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
												Assumed V/F = 0.64		
	Temperature	Weight % Feed	Av. B. P. of Fraction	Mol. Wt. of Fraction	Moles per 100 Grams Naphtha	Mole Fraction	Vapor Pressure, p	Reduced Temp., T_R	Mol. Wt. of Component	K at 14.7 lb./sq. in.	$K + L/V$ $(K + 0.562)$	1 / $K + 0.562$	1 / $K + 0.562$ Av.	Δz / $K + 0.562$
	° C.		° F.				Lb./sq. in.							
	82		179.6				137	0.87	93	7.3	7.862	0.1272		
	90	0.0	194		0.0064	0.0091	110	0.86	95	6.2	6.762	0.1479	0.1375	0.0013
	99	1.4	210	187	0.0143	0.0203	91	0.85	99	5.3	5.862	0.1706	0.1592	0.0032
	111	2.0	232	205	0.0196	0.0279	69	0.83	106	4.2	4.762	0.2100	0.1903	0.0053
	119	2.0	246	221	0.0187	0.0266	58	0.81	109	3.7	4.262	0.2346	0.2223	0.0059
	131	4.0	268	239	0.0357	0.0508	44	0.79	116	2.85	3.412	0.2931	0.2638	0.0134
	141	6.0	286	257	0.0508	0.0722	35	0.78	122	2.3	2.862	0.3494	0.3212	0.0232
	149	6.0	300	277	0.0483	0.0687	29	0.77	126	1.93	2.492	0.4013	0.3753	0.0258
	160	8.0	320	293	0.0615	0.0874	22	0.75	133	1.62	2.182	0.4583	0.4298	0.0376
	167.5	8.0	334	312	0.0592	0.0842	18.2	0.74	138	1.27	1.832	0.5459	0.5021	0.0423
	175.2	8.0	347	327	0.0714	0.1015	15.2	0.73	143	1.07	1.632	0.6127	0.5795	0.0588
	181	10.0	358	340	0.0417	0.0593	13.5	0.73	147	0.90	1.462	0.6840	0.6483	0.0384
	188	6.0	370	352	0.0402	0.0572	11.3	0.71	152	0.78	1.342	0.7451	0.7145	0.0409
	192.5	6.0	379	365	0.0327	0.0465	10	0.69	154	0.68	1.242	0.8051	0.7751	0.0360
	197.5	5.0	387	374	0.0321	0.0456	8.9	0.68	157	0.61	1.172	0.8532	0.8292	0.0378
	205	8.0	401	395	0.0497	0.0707	7.3	0.67	164	0.49	1.052	0.9506	0.9019	0.0638
	213	4.0	415	408	0.0239	0.0340	5.9	0.67	170	0.40	0.962	1.0395	0.9951	0.0338
	225	8.0	437	426	0.0457	0.0650	4.16	0.65	180	0.30	0.862	1.1601	1.0998	0.0715
	241	5.0	466	450	0.0270	0.0384	2.7	0.64	185	0.20	0.762	1.3123	1.2362	0.0475
	282	5.0	540	493	0.0243	0.0345	0.75	0.60	233	0.065	0.627	1.5948	1.4535	0.0501
					0.7032	0.9999								0.6366

16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
		Calculation of Liquid, Assumed V/F = 0.655					Liquid Accumulative		Calculation of Vapor, Assumed V/F = 0.655						Vapor Accumulative
$K + L/V$ $(K + 0.527)$	1 / $K + 0.527$	Av.	1 / $K + 0.527$ Av.	Δz	Mole fraction liquid, Δx	Wt. per mole liquid	Wt. fraction	Weight Fractions	$K + L/V$ $(K + 0.527)$	K	$K + 0.527$ Av.	Δz / $K + 0.527$	Vapor mole fraction, Δy	Mole fraction × mol wt.	Wt. fraction	Weight Fraction
7.827	0.1277							0.0000	7.827	0.9327						0
6.927	0.1444	0.1360	0.0012	0.0018	0.169	0.0011	0.0011	0.0011	6.927	0.9239	0.9283	0.0084	0.0128	1.20	0.0088	0.0088
5.827	0.1716	0.1580	0.0032	0.0049	0.480	0.0081	0.0042	0.0053	5.827	0.9096	0.9167	0.0186	0.0284	2.78	0.0205	0.0293
4.727	0.2115	0.1915	0.0053	0.0081	0.826	0.0053	0.0095	0.0148	4.727	0.8885	0.8991	0.0251	0.0382	3.90	0.0288	0.0581
4.227	0.2365	0.2240	0.0060	0.0092	0.984	0.0063	0.0158	0.0211	4.227	0.8753	0.8819	0.0235	0.0359	3.84	0.0284	0.0865
3.377	0.2961	0.2663	0.0135	0.0206	2.307	0.0149	0.0307	0.0360	3.377	0.8439	0.8596	0.0437	0.0669	7.49	0.0553	0.1418
2.827	0.3537	0.3299	0.0238	0.0363	4.283	0.0276	0.0583	0.0943	2.827	0.8136	0.8287	0.0598	0.0914	10.78	0.0796	0.2214
2.457	0.4070	0.3804	0.0261	0.0398	4.935	0.0319	0.0902	0.1262	2.457	0.7855	0.7996	0.0549	0.0839	10.40	0.0768	0.2982
2.147	0.4658	0.4364	0.0381	0.0581	7.553	0.0488	0.1390	0.1750	2.147	0.7545	0.7700	0.0675	0.1027	13.35	0.0986	0.3968
1.797	0.5565	0.5111	0.0430	0.0656	8.856	0.0572	0.1962	0.2322	1.797	0.7067	0.7306	0.0615	0.0938	12.66	0.0935	0.4903
1.597	0.6262	0.5913	0.0600	0.0916	12.824	0.0828	0.2790	0.3150	1.597	0.6700	0.6883	0.0699	0.1068	14.95	0.1104	0.6007
1.427	0.7008	0.6635	0.0393	0.0600	8.64	0.0558	0.3348	0.3708	1.427	0.6307	0.6504	0.0386	0.0588	8.47	0.0625	0.6632
1.307	0.7330	0.7168	0.0419	0.0639	9.521	0.0615	0.3963	0.4323	1.307	0.6029	0.6168	0.0353	0.0538	8.02	0.0592	0.7224
1.207	0.7968	0.7540	0.0371	0.0566	8.660	0.0559	0.4522	0.4882	1.207	0.5634	0.5832	0.0271	0.0414	6.33	0.0467	0.7691
1.137	0.8795	0.8540	0.0389	0.0594	9.266	0.0598	0.5120	0.5680	1.137	0.5365	0.5499	0.0251	0.0383	5.97	0.0441	0.8132
1.017	0.9833	0.9314	0.0658	0.1004	16.164	0.1043	0.6163	0.6723	1.017	0.4818	0.5091	0.0360	0.0549	8.84	0.0653	0.8785
0.927	1.0787	1.0310	0.0351	0.0536	8.951	0.0578	0.6741	0.7301	0.927	0.4315	0.4566	0.0155	0.0237	3.96	0.0293	0.9078
0.827	1.2092	1.1439	0.0744	0.1136	19.880	0.1283	0.8024	0.8584	0.827	0.3627	0.3971	0.0258	0.0394	6.90	0.0510	0.9588
0.727	1.3755	1.2923	0.0496	0.0757	14.004	0.0904	0.8928	0.9488	0.727	0.2751	0.3189	0.0122	0.0186	3.44	0.0254	0.9842
0.592	1.6891	1.5323	0.0529	0.0807	16.624	0.1073	1.0001	0.592	0.1098	0.1945	0.0067	0.0102	2.10	0.0155	0.9997
			0.6552	0.9999	154.927[a]	1.0001						0.6552	0.9999	135.38	0.9997	

[a] Calculated molecular weight.

vapor pressures in column 8, the reduced temperatures of column 9, and the molecular weights of column 10 as described. It is not necessary to determine K for each component directly. In complex mixtures all properties, including the equilibrium constants, K, may be considered continuous functions of the normal boiling points and log K as read from working charts such as Figures 5 and 6 may be plotted as a function of the normal boiling points of the components for purposes of interpolation as described.

Columns 12 through 15 are the calculations for the assumed value for V/F of 0.64, including the integration of Equation 13 on the assumption that the curve of the equation may be represented by short straight lines connecting the values corresponding to the components. The summation of the values in column 15 should equal the assumed value for V/F (0.64). The difference, 0.0034, is too large for a satisfactory solution in this case.

Columns 16 through 19 give similar data for the calculations based on an assumed value of 0.655 for V/F. The result, 0.6552, as indicated for the summation of column 19 is satisfactory.

Multiplying the values in column 19 by F/V gives the corresponding values for Δx or the composition of the liquid, L, in terms of normal boiling points (column 2) and mole fraction (column 20,

solution for Equation 13). Columns 21 through 23 indicate the calculations in converting mole fraction into weight fraction by use of the molecular weights of the fractions in column 5.

Columns 24 through 27 represent a check calculation on the quantity vaporized, using Equation 14. Multiplying the values of column 27 by F/V gives the values for Δy in column 28, or the composition of the vapor, V, which is converted to weight fraction as given in column 31.

A further check could be made by a material balance for each component in the feed, liquid, and vapor, or the moles of each component in the liquid could be determined by first computing the moles of each component in the vapor as in column 27 and subtracting these values from the moles of each component in the feed as given in column 7, thereby eliminating about one-third of the work.

The calculated average molecular weight of this California naphtha from column 6 of Table III is 100/0.7032 = 142, which is exactly the same as was experimentally determined by Brown and Caine (*10*).

The quantity of vapor as calculated by the assumption of ideal solutions (62.4 weight per cent) is in good agreement (apparently within the experimental error) with the experimental value of 60.2 weight per cent as shown in Table IV.

The quality of the vapor as calculated is compared with the experimental data in Table V and shown to be in excellent agreement. An apparent error of 1.5 per cent in the experimental data is indicated by the difference of 60° F. between the initial boiling points of the feed and vapor.

Table IV. Comparative Results on Quantity of Vapor from Equilibrium Vaporization of a California Naphtha

	Feed Vaporized at 350.6° F. (177° C.) and 760 mm.	
	Mole %	*Wt. %*
Experimental (*10*)	63.4	60.2
Raoult's law	65.7	62.6
Raoult's law modified (*10*) by $k = 0.9$	50.5	47
Ideal solution K	65.5	62.4
Empirical method	61.0	58.0

Table V. Comparative Results on Quality of Vapor from Equilibrium Vaporization of a California Naphtha

	Normal Boiling Points			
			Vapor calcd.	
From True B. P. Curve	Feed, exptl. (*10*)	Vapor, exptl. (*10*)	as ideal soln.[a]	Vapor calcd. empirically[b]
Wt. %	*° F.*	*° F.*	*° F.*	*° F.*
0	180	122	180	...
5	240	220	227	225
10	268	251	253	253
20	295	278	281	280
30	320	300	301	300
40	335	319	321	320
50	350	331	334	332
60	370	348	347	345
70	387	363	365	361
80	408	383	383	381
90	437	415	410	414

[a] Using K as from Figure 3.
[b] From Figure 9.

Because each component is carried throughout the entire computation as an individual, it is possible, by a simple modification of the calculations indicated in Table III, to calculate the quantities and qualities of liquid and vapor formed from each of two or more feeds vaporized in a common vessel in the presence of each other.

This method has been used with equally satisfactory results in computing equilibrium vaporization at high temperatures and pressures. The effect of fixed or noncondensed gases on the vaporization can be accurately calculated from their composition and properties in the same manner as the working charts give values for K above the critical temperature (*14*).

Through the courtesy of Doctor Bahlke of the Standard Oil Company (Indiana) the authors were supplied with samples of naphtha and gasoline prepared from the same stock and of approximately the same A. S. T. M. distillation as those used in previous pressure-volume-temperature studies by Bahlke and Kay (*4*). The new sample of gasoline was 59° compared with 57.3° A. P. I. for the original (*4*), and the new sample of naphtha was 56.8° A. P. I. compared with 57.1°.

Accurate laboratory column distillations were made on these samples, taking gravities of each 5 per cent cut. Molecular weights of various fractions were determined. From these data the points given in Table VI were determined in the same manner as outlined in Table III.

The agreement is as good at higher as at lower pressures. The values for K as determined from Figure 3 or from the corresponding working plots were used directly without correction of any kind in these calculations. Any correction for deviation from ideal solutions would increase the values of K for the more volatile components and decrease the calculated temperatures for the small percentages vaporized, thereby making for better agreement.

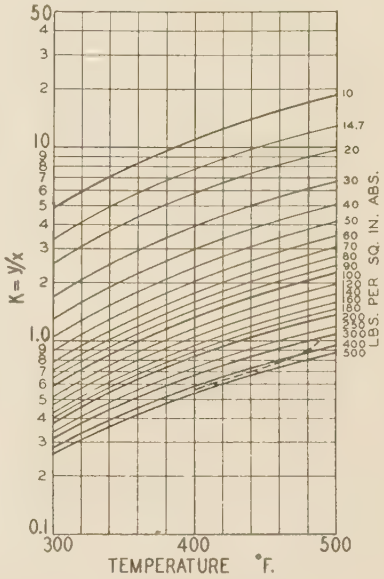

Figure 6. Part of *N*-Heptane Chart

Table VI. Comparison of Experimental and Calculated Vaporizations of a Naphtha and a Gasoline

		Temperature				Temperature	
		59° A. P. I. gasoline	57.3° A. P. I. gasoline			56.8° A. P. I. naphtha	57.1° A. P. I. naphtha
Vapor	Abs. Pressure	(calcd.)	(exptl.)	Vapor	Abs. Pressure	(calcd.)	(exptl.)
Wt. %	*Lb./sq. in.*	*° F.*	*° F.*	*Wt. %*	*Lb./sq. in.*	*°.F.*	*° F.*
0	365	500	491	0	57.3	350	340
0	51.5	250	230	0	211	500	485
38.4	260	500	490	100	41	350	345
87	200	500	504	100	189	500	492
100	28	350	360				
100	180	500	508				

Calculation of Equilibrium Curves

Equilibrium curves of the type suggested by Obryadchakoff (*56*) may be readily and accurately calculated from the composition of the vapor or of the liquid. These equilibrium curves are constructed by plotting along the ordinate the percentage of material boiling below any temperature ($T°$) in the vapor and along the abscissa the percentage of material boiling below the same temperature ($T°$) in the liquid in equilibrium with the vapor. This method assumes that for equilibrium purposes any complex mixture may be considered as composed of two components, one representing all the material boiling below any chosen temperature and the other representing all the material boiling above this temperature in either liquid or vapor. Obryadchakoff has indicated that a single equilibrium curve may be used for any pair of such components for a given mixture. These curves are a most convenient means for expressing equilibrium compositions of vapor as a function of that of the liquid, since they simplify all complex mixtures to equivalent binary mixtures.

These curves may be constructed in an accurate and convenient manner by means of the equilibrium constants, using

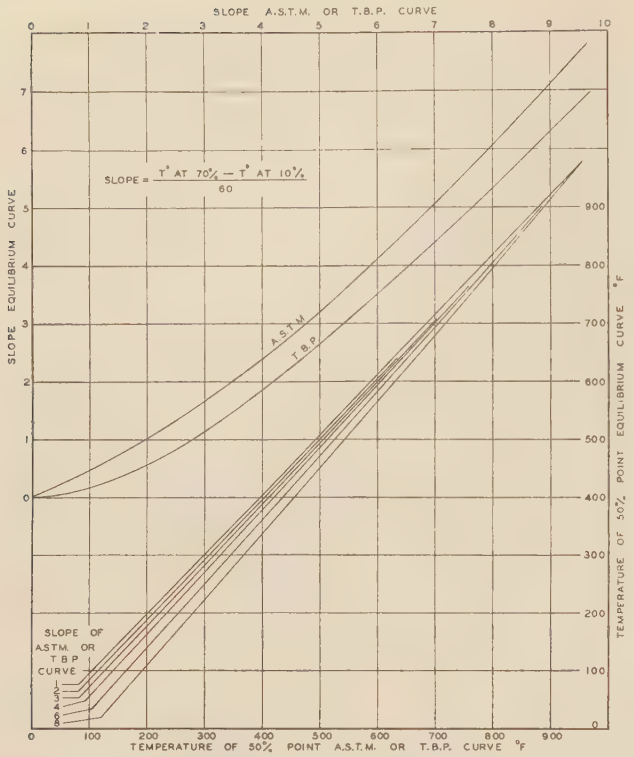

FIGURE 7. EMPIRICAL METHOD FOR DETERMINING EQUILIBRIUM VAPORIZATION CURVE

(T. B. P. = true boiling point)

Equation 15 for calculating mole fraction in vapor (y) as a function of mole fraction in liquid (x) boiling below the same temperature. Equation 25 may be used in the same manner when the composition of the vapor is known in terms of a boiling point analysis. The integrals of the curves of K as a function of x or of $1/K$ as a function of y give the equilibrium curve directly, as both integrals must equal unity.

If it is desirous to find the weight per cent composition of a vapor from a weight per cent curve of the liquid, the following relationship holds:

$$\int_0^1 dy' = \frac{M_L}{M_V}\int_0^1 K\,dx' = 1 \qquad (25)$$

in which dy' = weight per cent of the differential component in the vapor
dx' = weight per cent of same component in the liquid
M_L = average molecular weight of liquid
M_V = average molecular weight of vapor

This equation appears to require the molecular weights of the vapor and liquid for its solution, but the fact that M_L/M_V times the integral equals unity at equilibrium makes it possible to solve the equation without the knowledge of either molecular weight. The ratio of the molecular weights may be calculated from the integral evaluated between limits of zero to one and be applied to the integrals for all the intermediate values of x'.

The corresponding equation for computing the composition of the liquid:

$$\int_0^1 dx' = \frac{M_V}{M_L}\int_0^1 \frac{dy}{K} = 1 \qquad (26)$$

may be utilized in a similar manner.

EMPIRICAL METHODS

Because of the greater convenience many empirical methods have been proposed for estimating vapor pressure and vaporization characteristics of petroleum fractions from their A. S. T. M. or true boiling point distillation curves. Although seldom as exact as the theoretical relationships discussed above, they have been widely used because of their great convenience.

The vapor pressures of fractions within the gasoline range may be estimated from the 10 per cent point on the A. S. T. M. distillation by the following formula (*8*):

$$\log \frac{p}{760} = (3.41 + 2.11 \times 10^{-3}T_{10} - 0.33S)\left(1 - \frac{T_{10}}{T}\right) \qquad (27)$$

where p = vapor pressure
T = ° Rankine at which vapor pressure is desired
T_{10} = ° Rankine 10% point in A. S. T. M. distillation
S = slope, ° F. per % A. S. T. M. at 10% point

The dew point is closely related to the 90 per cent point on the A. S. T. M. distillation (*9*) and may be estimated from the following equation (*7*):

$$\frac{\text{Abs. temp. of 90\% point on A. S. T. M. distn.}}{\text{Abs. temp. of dew point}} = 1.084 \qquad (28)$$

The dew points of the fuel mixed with various ratios of air have been carefully studied and may be estimated from the A. S. T. M. distillation data in much the same manner (*6*, *9*, *12*, *72*). For fractions heavier than gasoline, relationships are uncertain but the dew points seem to be related more closely to the 85 and 75 per cent points than for the 90 per cent point, as is the case with gasoline (*80*), and the bubble point is related to percentages greater than 10. Nelson (*53*) relates the bubble point to the 50 per cent point for side streams from a topping column.

The amount of liquid and vapor formed in an equilibrium vaporization at atmospheric pressure is usually expressed as an equilibrium vaporization curve which shows the percentage of vapor formed in an equilibrium vaporization as a function of temperature. An empirical relationship between the equilibrium vaporization curve and the A. S. T. M. and the true boiling point curves was found to exist by Piroomov and Beiswenger (*59*). The equilibrium vaporization curve was assumed to be a straight line and its slope was found to be related to the slope of the A. S. T. M. or true boiling point distillation curve between the 10 and 70 per cent points. The point of intersection of the equilibrium vaporization curve with the A. S. T. M. or true boiling point curve was related to the 50 per cent point on the distillation curve and the slope of the distillation curve.

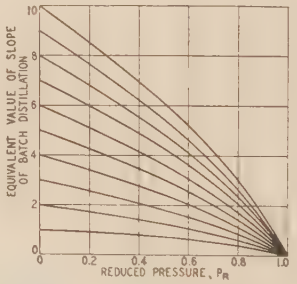

FIGURE 8. CORRECTION OF SLOPE OF EQUILIBRIUM VAPORIZATION CURVE FOR DIFFERENT PRESSURES

Use the equivalent slope of the batch distillation as indicated in this figure for determining the slope of equilibrium vaporization curve (if the pressure of vaporization is other than atmospheric) for use with Figures 7, 9, and 10:

$$\text{Slope} = \frac{T° \text{ at 70 per cent} - T° \text{ at 10 per cent}}{60}$$

For pressures greater than atmospheric it was suggested that the point of intersection be raised according to the vapor pressure curve of a pure hydrocarbon.

A similar but somewhat more convenient type of plot suggested by Nelson and Souders (*54*) has been constructed

on the basis of all available data. This plot (Figure 7) relates the slope of the equilibrium vaporization curve to the slope of the batch distillation curve, and the 50 per cent point of the equilibrium vaporization curve to the 50 per cent point of the batch distillation curve with a correction for the slope of the latter.

The use of Figure 7 may be demonstrated by application to the same California naphtha (*10*). The slope of the true

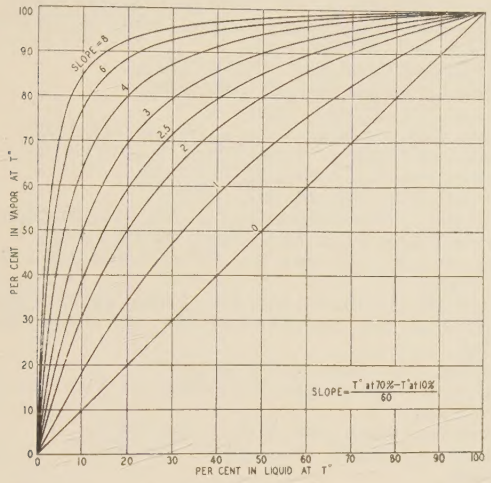

Figure 9. Equilibrium Curve for True Boiling Point or Column Distillation Data

Figures on curves indicate slope of distillation curve of feed:

$$\text{Slope} = \frac{T° \text{ at 70 per cent} - T° \text{ at 10 per cent}}{60}$$

boiling point curve between the 10 and 70 per cent points is 2° F. per per cent, and the 50 per cent point is 350° F. from data in Table V.

From the slope (2° F. per per cent) of the true boiling point curve, the slope of the equilibrium vaporization curve is found to be 0.52. The 50 per cent point of the equilibrium vaporization curve is 346° F. as determined from the 50 per cent point and the slope of the true boiling point curve. To find the percentage vaporized in a vaporization at 350.6° F., locate the 50 per cent point of the equilibrium vaporization curve at 346° F. and draw a line through this point with a slope of 0.52° F. per per cent. The intersection of this vaporization line with 350.6° F. at 58 per cent indicates that 58 per cent vapor would be formed compared with 60.2 per cent as determined experimentally (Table IV).

Similar methods are applied in using the relationship between the equilibrium vaporization curve and the A. S. T. M. distillation, using the proper curve for the relationships between the slopes.

For estimating the equilibrium vaporization curves at higher or lower pressures, the 50 per cent point of the equilibrium vaporization curve may be modified according to the vapor pressure curve of a pure hydrocarbon, and the slope obtained by applying the correction indicated in Figure 8 to the slope of the batch distillation. The curves shown in Figure 8 were derived from limited data but their use is justified until more accurate data are available.

In estimating the quality of vapor and liquid formed in an equilibrium vaporization, empirical equilibrium curves of the type suggested by Obryadchakoff (*56*) may be used with satisfactory results in most cases, particularly relatively close-cut fractions.

A relationship has been found between the slope of this equilibrium curve and the slope of the batch distillation curve of the feed material. The available data have been carefully analyzed, and equilibrium curves based on true boiling point distillation curves are indicated in Figure 9, and similar curves based on A. S. T. M. distillation data are given in Figure 10. The numbers on the curves indicate the slope between 10 and 70 per cent on the batch distillation curve of the feed for which the equilibrium curve may be used. These curves are based upon equilibrium conditions at atmospheric pressures but may be used for other pressures by using a curve corresponding to a different slope for the batch distillation as indicated in Figure 8.

From a knowledge of the quantity of vapor and liquid formed in an equilibrium vaporization as determined from Figures 7 and 8, the quality of the vapor and liquid expressed as a distillation curve can be obtained from the composition of the feed by use of Figures 9 or 10 in the following manner: The percentage of the vapor as indicated along ordinate y and the percentage of the liquid as indicated along abscissa x will distill at temperature t on the true boiling point curve of the feed, corresponding to the percentage of the feed equal to $yV + xL$, where V and L represent percentage total vapor and percentage total liquid based on feed. This percentage of the feed is obtained by multiplying the percentage of the vapor as indicated on ordinate y by the percentage of feed

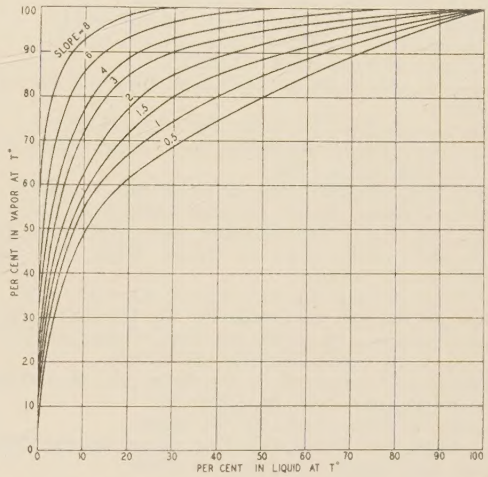

Figure 10. Equilibrium Curve for A. S. T. M. Distillation Data

Figures on curves indicate slope of A. S. T. M. distillation curve of feed:

$$\text{Slope} = \frac{T° \text{ at 70 per cent} - T° \text{ at 10 per cent}}{60}$$

vaporized, and adding to this product the product of the corresponding abscissa x by the percentage of feed left as a liquid in the equilibrium vaporization. This sum is the percentage of the feed distilled at temperature t in the batch distillation of the feed.

Example. The quantity of vapor formed in the equilibrium vaporization of the same California naphtha (*10*) was determined in the manner indicated as 58 per cent. In order to introduce no extraneous error, the experimental value of 60 per cent for this naphtha is used in this demonstration. Equilibrium curve 2 in Figure 9 is used because the slope of the batch distillation curve was 2° F. per per cent. Fifty per cent of the vapor is distilled at the same temperature as 20 per cent of the liquid residue. Fifty per cent of the vapor is 30 per cent of the feed because the total vapor is 60 per cent of the feed. Twenty per cent of the liquid is 8 per cent of the feed because the total liquid is 40 per cent of the feed. Therefore the temperature of 50 per cent of the vapor and 20 per cent of the liquid is that of 30 + 8 or 38 per cent of the feed. From the distillation curve of the feed this is found to be 332° F.

The results for the quality of vapor determined in this manner are compared with the experimental results, and those computed by the theoretical method, in Table V. The agreement in this case is better than may usually be expected.

OTHER APPLICATIONS

These principles and methods are of wide application to all types of vaporization processes, only a few of which have been demonstrated. The application of the thoretical methods to natural gasoline absorption and fractionation has been treated (*13*). The same theoretical methods as applied to complex mixtures may be used for studies in fractionation of petroleum products at all pressures. The extremely simple application of the equilibrium curves (*56*), Figures 9 and 10, to distillation problems of complex mixtures, making possible all the simplifications of the graphical method of McCabe and Thiele (*50*) for binary mixtures may not be theoretically exact but is justified in many cases, and appears satisfactory for fractionation even at high pressures.

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